

PATENT SPECIFICATION

L196.597



NO DRAWINGS

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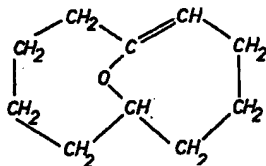
COMPLETE SPECIFICATION

Preparation of an Oxido-Cyclodecene

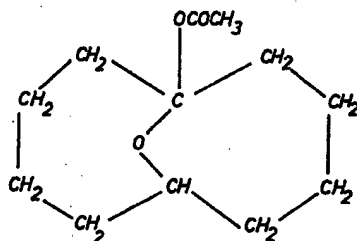
We, GEIGY (U.K.) LIMITED, a British Company, whose Registered Office address is Simonsway, Manchester 22, Lancashire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to processes of producing cyclic olefine derivatives and in particular to processes of producing 1,6-oxido-cyclodec-1-ene.

According to the present invention, there is provided a process for the production of 1,6-oxido-cyclodec-1-ene having the formula I:—



comprising pyrolysing 1 - acetoxy - 1,6-oxidocyclodecane having the formula II:—



at a temperature of up to 450°C.

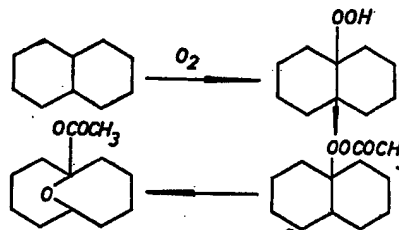
The pyrolysis procedure may be carried out, for instance, by slowly adding the 1-acetoxy-1,6-oxido-cyclodecane to a reactor, maintained at the pyrolysis temperature and fitted for distillation. The distillation product may be further purified, for instance, by fractional

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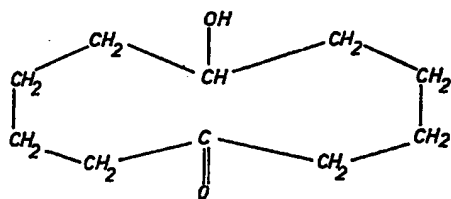
distillation under reduced pressure, if desired.

At temperatures substantially in excess of 450°C., it has been found that a considerable proportion, for instance, up to 50% by weight, of the starting material is converted to unknown materials, the remaining 50% of the product being the desired 1,6-oxido-cyclodec-1-ene. On the other hand, at temperatures much below 400°C., although little starting material is lost and the only major product is 1,6-oxido-cyclodec-1-ene, only a comparatively low rate of conversion of starting material to the desired product is achieved. Accordingly, in order to achieve an acceptable rate of conversion combined with a reasonably high yield of 1,6-oxido-cyclodec-1-ene, it is preferred to effect the pyrolysis at a temperature within the range of from 400°C. to 450°C.

The 1 - acetoxy - 1,6 - oxidocyclodecane which is employed to produce 1,6-oxido-cyclodec-1-ene may be obtained, for example, by the oxidation of decalin to decalin peroxide, followed by esterification of the peroxide with acetic anhydride to form decalol peracetate and finally rearrangement of the decalol peracetate to 1 - acetoxy - 1,6 - oxidocyclodecane. This method is described by Muller and Pfluger, *Kunststoffe* (1960), 50, page 205 and the reaction is said to proceed according to the following reaction scheme:—



The 1,6 - oxido - cyclodec - 1 - ene may also be produced by treating 6-hydroxycyclodecanone having the formula:—



with an acid catalyst at an elevated temperature until all the water formed during the reaction has been removed.

5 The reaction is advantageously carried out in the presence of an inert organic solvent such as benzene, toluene or xylene; the use of such a solvent serves as a convenient means of removing continuously water formed during the reaction in the form of an azeotropic mixture. If desired, the 1,6-oxido-cyclodec-1-ene may be isolated in a pure state by conventional means such as removal of inert solvent by distillation, solvent extraction of the residue, washing of the solvent extract and finally distillation of the washed extract.

The acid catalyst may be for example concentrated sulphuric acid or phosphoric acid but is preferably p-toluene sulphonic acid.

20 If an inert solvent is employed for producing 1,6 - oxido - cyclodec - 1 - ene, the reaction is conveniently effected at the reflux temperature of the solution; the reflux temperature normally being within the range of from 100° to 250°C.

25 Alternatively, the 1,6 - oxido - cyclodec-1-ene may be produced from 6-hydroxycyclodecanone by the process described and claimed

in British Patent Specification No. 979,889.

The 1,6 - oxido - cyclodec - 1 - ene produced according to the process of the present invention is a useful intermediate in organic chemistry particularly for the production of 5 - hydroxy - 1,10 - decanedioic acid-1,6-lactone according to the process described and claimed in our copending British patent application No. 21512/68 (Serial No. 1,196,595).

The following Examples further illustrate the present invention. Parts by weight bear the same relation to parts by volume as do kilograms to litres.

EXAMPLES 1 and 2

Production of 1,6-oxido-cyclodec-1-ene.

21.2 parts of 1-acetoxy-1,6-oxido-cyclodecane were added dropwise into a reactor maintained at 400°C., and fitted for distillation at atmospheric pressure. The addition of the starting material was complete after 90 minutes, after which time the distillate was taken up in ether, washed with dilute alkali and then with water to remove acetic acid. The ether was evaporated, the residue distilled under reduced pressure and the distillate weighed and analysed by gas/liquid chromatographical (G.L.C.) means. The results obtained for this experiment and a similar experiment are shown in the following Table. The Table also contains, for comparative purposes only, details of a similar experiment conducted at a temperature outside the scope of this invention, that is 500°C.

TABLE

| Pyrolysis temperature (°C) | Addition time (minutes) | Starting material (2) consumed (%) | Yield of (1) based on (2) consumed (%) | Parts by weight of distillate | GLC analysis % composition of distillate | | |
|----------------------------|-------------------------|------------------------------------|--|-------------------------------|--|----|----|
| | | | | | 1 | 2 | 3 |
| 400 | 90 | 42 | 57 | 15.2 | 23 | 76 | 1 |
| 450 | 35 | 62 | 81 | 15.9 | 48 | 50 | 2 |
| 500 | 30 | 99 | 41 | 12.6 | 49 | 2 | 49 |

Key to numbers used in Table:

1 = 1,6-oxido-cyclodec-1-ene

2 = 1-acetoxy-1,6-oxido-cyclodecane

3 = unknowns.

65 The results in the Table show well the advantage of working at temperatures of about 450°C., in order to combine a reasonable degree of conversion with a high degree of selectivity in obtaining the desired product.

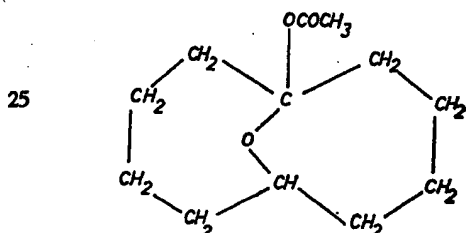
EXAMPLE 3

117.7 parts of 6-hydroxycyclodecanone, 1.0 parts of p-toluene sulphonic acid and 700 parts by volume of benzene were placed in a reactor fitted with a stirrer, a thermometer

and a conventional device for collecting the distillate and continuously separating water produced therein. The reaction mixture was heated under reflux conditions for 24 hours, and during this time 12 parts by volume of water (the theoretical quantity) was collected. All or substantially all of the benzene solvent was then removed by distillation under reduced pressure. The residue was taken up in an excess amount of diethyl ether and this solution was washed with 5% aqueous solution of sodium hydroxide and then with water. Removal of the ether solvent followed by fractional distillation gave 99.5 parts of a product boiling at 91°C., at a pressure of 8 millimetres of mercury, representing a yield of 95% theoretical. Gas/liquid chromatographical examination of the product showed it to contain 98.4% by weight of 1,6-oxido-cyclodec-1-ene.

WHAT WE CLAIM IS:—

1. A process of producing 1,6-oxido-cyclodec-1-ene comprising pyrolysing 1-acetoxy-1,6-oxidocyclodecane having the formula:—



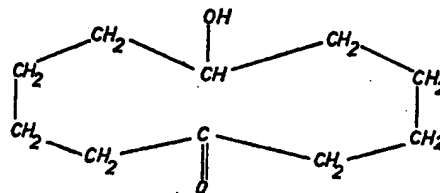
at a temperature of up to 450°C.

2. A process as claimed in Claim 1 wherein the 1-acetoxy-1,6-oxido-cyclodecane is slowly added to a reactor maintained at the pyrolysis temperature and fitted for distillation.

3. A process as claimed in Claim 1 or 2 wherein the pyrolysis is effected at a temperature within the range of from 400°C. to 450°C.

4. A process of producing 1,6-oxido-

cyclodec-1-ene comprising treating 6-hydroxycyclodecanone having the formula:—



with an acid catalyst at an elevated temperature.

5. A process as claimed in Claim 4 wherein the process is continued until all the water formed in the reaction has been removed.

6. A process as claimed in either of Claims 4 or 5 wherein the acid catalyst is p-toluene sulphonic acid.

7. A process as claimed in Claim 4 or 5 wherein an inert organic solvent is used which forms an azeotropic mixture with water.

8. A process as claimed in Claim 7 wherein the organic solvent is benzene, toluene or xylene.

9. A process as claimed in any of Claims 4 to 8 wherein the 1,6-oxido-cyclodec-1-ene is isolated in a pure state by removal of solvent by distillation, solvent extraction of the residue, washing of the solvent extract and finally distillation of the washed extract.

10. A process as claimed in any of Claims 7 to 9 wherein the process is effected at the reflux temperature of the solution.

11. A process as claimed in Claim 10 wherein the reflux temperature is within the range of from 100° to 250°C.

12. A process of producing 1,6-oxido-cyclodec-1-ene substantially as described in any of the Examples.

13. 1,6-Oxido-cyclodec-1-ene whenever produced by a process claimed in any of the preceding claims.

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